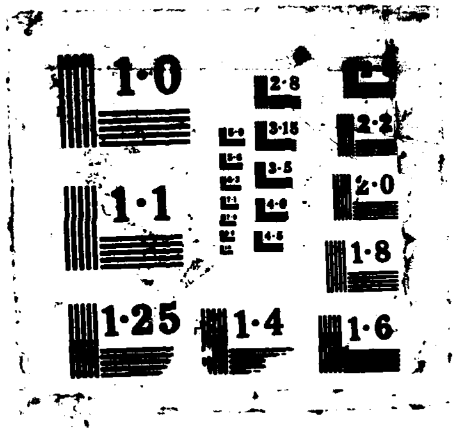
AD-A185 258 DEVELOPMENT OF A LOW NOISE 10 K J-T REFRIGERATION SYSTEM(U) MMR TECHNOLOGIES INC MOUNTAIN VIEW CA W A LITTLE 15 FEB 87 N00014-86-C-0301 1/1

UNCLASSIFIED F/G 13/1 NL


1·0
2·8
3·15
3·5
4·0
4·5
2·2
2·0
1·1
1·8
1·25
1·4
1·6

Item No. 0001AB

Technical Progress Report

Development of a Low Noise 10 K J-T Refrigeration System

(1)

Item No. 0001AB

Technical Progress Report

Development of a Low Noise 10 K J-T Refrigeration System

February 15, 1987

MMR Technologies, Inc.
1400 Stierlin Rd, #5
Mountain View, CA 94043

Prepared by :

William A. Little
Chairman

TABLE OF CONTENTS

1.0 Introduction

This report summarises work done on Contract No. N00014-86-C-0301 in the period from August 15, 1986 to February 15, 1987 on the development of a low noise Joule-Thomson, microminiature refrigeration system designed for 10 K operation.

Two events have occurred since the last report which have had an important influence on the direction of this program. The first was the confirmation through a series of experimental measurements of the remarkable cooling power at 80 K to 90 K of the nitrogen-hydrocarbon gas mixtures discussed briefly in the previous report. These experiments confirmed that these mixtures could give a refrigeration capacity in a Joule-Thomson refrigerator an order of magnitude greater than that attainable with argon or nitrogen at the same input pressures. In addition, it was recognised that this high efficiency allowed one to use a heat exchanger of substantially smaller surface area and a compressor designed for operation at much lower pressures. This lower pressure operation would greatly reduce the wear of the piston seals and thereby prolong the life of the system. It was also discovered in the course of these measurements that the use of the gas mixtures resulted in virtually clog-free operation of the refrigerators. This result is attributed to the remarkable ability of the mixture to solubilize many condensible impurities such as compressor lubricants, carbon dioxide and to some extent water vapour, which normally would condense out in the cold end of the J-T heat exchanger and clog the refrigerator.

While the properties of these gas mixtures have been known for more than a decade, no military or commercial use has been made of them because the mixtures are flammable and in some concentrations in air, explosive. It occurred to us that the remarkable solvent behaviour of the mixtures might provide a way around this handicap. We report how this has been accomplished successfully through the development of a mixture which has similar cooling properties but is non-flammable. A patent application has been filed on the use of such gas mixtures for refrigeration use. This work was done as part of another study but it immediately became evident that it would have a major impact upon the work of this contract. This work is being prepared for publication.

The other event, which has influenced the direction of the work of the program, was the recent discovery of superconductivity in the $La(Sr)CuO_4$ series of compounds at temperatures exceeding 40 K. This put added importance to the development of an efficient, low noise refrigeration system for the temperature range between 80 K and 20 K for use with these superconducting materials.

These two developments have brought to focus the need for a better understanding of gas mixtures as these can be expected to play a major role in any future system requiring low noise refrigeration below 80 K. In order to develop a rational design of a refrigerator for use with these gases it was imperative to expand further the work on determining their phase diagrams. A four or five component gas mixture can be expected to have an enormously complicated phase diagram. To determine it empirically, as a function of composition, would be a heroic undertaking, more suited to a long term program at the Bureau of Standards ,than for a program focussing on the practical use of the gas. However, the possibility of developing a useful theoretical model had been shown to be possible and would involve much less effort than a full blown experimental study.

In this report we present the results of preliminary measurements using a particular gas mixture in a standard MMR refrigerator showing the cooldown behaviour and the capacity in comparison with nitrogen. Next we present the results of the theoretical work on the determination of the phase diagram for that mixture which had been used in the above experiments. The isobars and isenthalps have been determined as a function of the temperature and entropy of the mixture. The expression for the enthalpy and pressure as a function of temperature and density has allowed us to determine analytically the work of compression, in this case, assuming isothermal compression. From this, the efficiency of an ideal refrigerator has been determined, relative to that of a Carnot refrigerator. It is shown that extremely high efficiencies are attainable.

We present results of the operation of an MMR refrigerator with the gas mixture at reduced pressures. Satisfactory operation down to 700 psi was achieved.

These new results and the benefits which would accrue from the use of the gas mixture in the first stage of the three stage refrigerator have lead us to reconsider the design of both the refrigerator and the compressor. We report on the changes planned and what progress has been made to implement these changes.

2.0 Gas Mixtures

2.1 Experimental

Preliminary experiments had been done using a mixture of nitrogen and hydrocarbons of the following approximate composition by volume at STP.

Propane	10%
Ethane	19.98%
Methane	40.09%
Nitrogen	29.93%

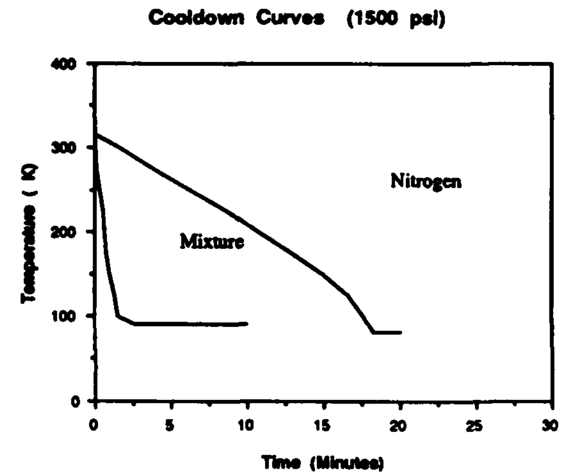


Figure 2.1 Cooldown Curves for Nitrogen and for the gas mixture.

This mixture was shown to provide cooling in a J-T refrigerator to about 82 K and a refrigeration capacity of 6 to 9 times that of nitrogen at the same pressure. However, the gas was flammable and in mixtures with air is explosive. It was known, however, that the gas could solubilize many condensible impurities such as carbon dioxide and the higher hydrocarbons at temperatures down to 80 K. It was also known that a few percent of the fire retardant CF_3Br, known commercially as Halon, added to a hydrocarbon gas renders it non-flammable. However, Halon freezes at 105 K so the addition of it to a hydrocarbon mixture to render it non-flammable, for use in a J-T refrigerator, might be expected to cause the refrigerator to clog when operated below this temperature. We argued, however, that use with the nitrogen-hydrocarbon gas mixture might be possible nevertheless, if the mixture could keep the Halon in solution in the same way that it solubilizes other condensibles. This was tried and found to be true. It was found that a 3% addition of Halon to the nitrogen-methane-ethane-propane mixture rendered it completely inert, yet allowed operation in a J-T refrigerator to temperatures below 76 K without clogging and with a capacity seven to ten times that of nitrogen gas at the same input pressure.

A mixture of these gases was prepared and the cooldown rate and refrigeration capacity of a standard MMR refrigerator measured with the mixture and with nitrogen. For the same input pressure the results for the two gases were compared. The results obtained are shown in figures 2.1 and 2.2. The advantage of the use of the mixture for cooling to the 80 K to 90 K temperature region is evident. Two factors should be noted in comparing these two curves. First we note that the slope of the initial ramp for the capacity vs temperature is the same for the mixture as it is for the nitrogen. The slope of this ramp, 18 K/Watt is determined by the thermal resistance of the glass layer which lies between the alumina substrate upon which the heater and temperature sensor are mounted and the boiling liquid. The use of a highly conductive substrate in direct contact with the liquid should allow the dissipation of 2.0 to 2.5 Watts/cm^2 at the cold

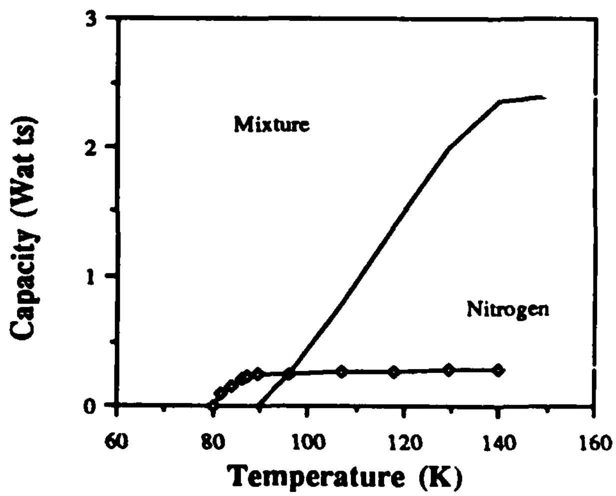


Figure 2.2 Refrigeration Capacity for Nitrogen and gas mixture

end of such a refrigerator with only a few degrees rise in temperature.

Second, we note that the minimum temperature observed with the mixture was 90 K with an input pressure of 1500 psi. This was attributed to a large back pressure at the boiler of the refrigerator. This was confirmed by noting that the temperature fell to 84.9 K on reducing the pressure to 700 psi. On a different refrigerator, a temperature of 82.4 K was observed at 700 psi input pressure, and at reduced pressure by pumping on the outlet of the refrigerator, a temperature of 77.0 K.We understand this in the following way. At the lowest temperatures one can expect the liquified gas, containing hydrocarbon components such as propane and ethane at a temperature 100 K or more below their boiling points, to be much more viscous than liquid nitrogen. The flow of this fluid through the outflow heat exchanger could be expected to cause a considerable back pressure at the boiler and consequently to cause a rise in the temperature of the boiler. Reducing the flow by reducing the pressure should reduce the temperature as observed. The back pressure can be reduced by modifying the design of the refrigerator accordingly.

2.2 Determination of Phase Diagrams

In 1940 Benedict, Webb and Rubin[1] (BWR) proposed an equation of state which has since been found to be successful in describing the temperature and pressure dependence of the entropy and enthalpy of light hydrocarbons such as methane, ethane, propane and other gases including nitrogen. This was successful in accounting for these properties in both the liquid and the gaseous state and in the viscinity of the critical point. Moreover, they showed that the numerical parameters in the BWR equations which are needed to describe the properties of mixtures of the gases could be derived from a knowledge of the properties of the pure gases, and that the use of these parameters allowed one to derive the entropy and enthalpy values for arbitrary mixtures of these gases. The results obtained were found to agree well with experimental values. They also showed how these equations could be used to determine the liquid-vapor equilibria for these mixtures.

At the time this work was done, computing facilities were primitive and extremely time consuming. We realised that these equations could readily be programmed on a PC to allow the rapid determination of those thermodynamic quantities needed for the design of J-T refrigerators using gas mixtures. Preliminary work done in August 1986 confirmed the feasibility of this approach. Al Nash, a recent graduate from the Physics Department at Stanford working with Dr. Little at MMR succeeded in developing a computer program to determine the entropy, enthalpy and pressure of the gas as a function of the temperature and density. Results were checked with experimental values and found to yield good agreement over most of the region of interest. With the help of Frank Kenter this has now been developed into a full fledged program to determine automatically the isobars, isenthalps and isochores for arbitrary mixtures of the gases methane, ethane, propane and nitrogen. It may readily be extended to include other gases.

In Figure 3 we show the results obtained for a gas mixture used in other experimental work, having the composition:

Propane	4.0%
Ethane	27.7%
Methane	39.5%
Nitrogen	28.8%

One should note that from 300 K in a simple expansion from 300 atm. to 1 atm., the gas cools to 175 °C. In addition it can be seen that significant cooling occurs for an expansion from 50 atm.

The results from these calculations have been tabulated. We are now begining a systematic study of the effects of varying the composition of the gas. We had noted earlier that quite small changes in the relative composition of the components made substantial differences to the refrigeration capacity of the refrigerators.

One of the most important consequences of the rapid drop in enthalpy with pressure shown in the figure is that efficient cooling can be obtained with heat exchangers of much smaller surface area than those necessary for use with nitrogen or argon. This makes possible a more compact design of the first stage of the refrigerator and releases "real estate" for the more critical

hydrogen and helium stages.

2.3 Estimate of Efficiency

In order to obtain an estimate of the power required for the operation of a refrigerator between 300 K and 90K we have calculated the work required to compress the gas isothermally from 1 to 100 atm. at 300 K by integrating the BWR equations. In this range the gas behaves much like an ideal gas and one obtains a figure of 11,241joules / mole. The maximum amount of heat which the refrigerator can absorb at the lowest temperature is the difference in enthalpy between the outlet gas at 1 atm.at 300 K and the inlet gas at 100 atm. at 300 K assuming a heat exchanger of 100 % efficiency. Actual exchangers presently in use have an efficiency of 96% - 98 %. The difference of enthalpy can be read off the figure or tables and when converted to similar units gives 2,626 joules/mole. This yields a figure for the efficiency of 78% relative to Carnot. One must be a little cautious of this result because, unlike a J-T refrigerator operated with a pure gas, with a mixture, the absorption of heat can occur at intermediate temperatures and if the lower stage is starved of fluid due to too low a fraction of the lowest boiling point component being present, the outlet gas can then emerge cold even with a 100% efficient heat exchanger. The above enthalpy figures then would need to be adjusted to take in to account the temperature of the outlet gas. However, we have noted experimentally that the temperature of the outlet gas is close to that of the inlet gas and consequently the above estimate should be valid.

One can understand the high efficiency figure by noting that the gas mixture behaves much like a cascade refrigerator with each component operating in a vapor-compression-like cycle after being precooled by the expansion of the higher boiling components. It is well known that in such vapor-compression cycles efficiencies of 70% - - 90 % relative ti Carnot are attainable.

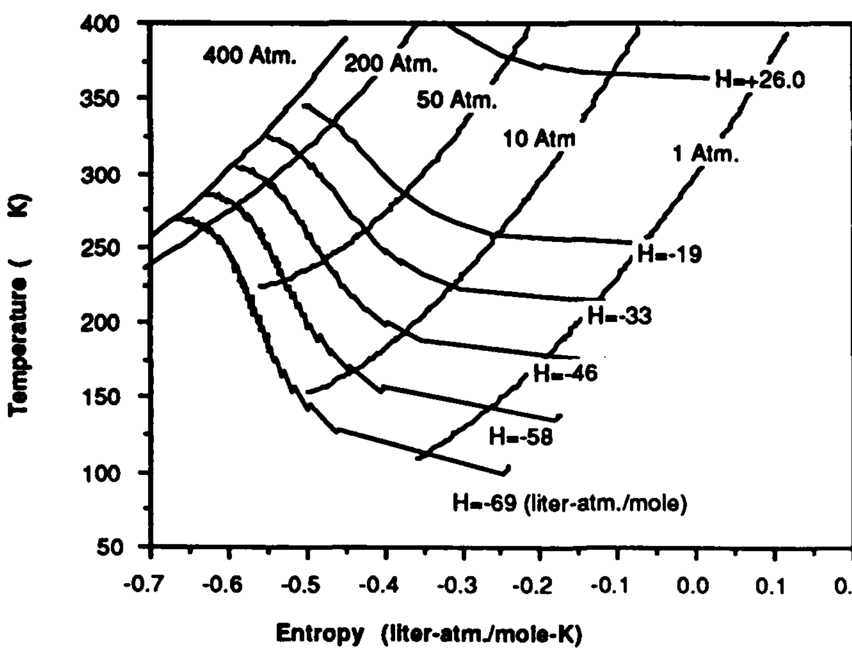


Figure 3.0 Calculated Values for the Entropy, Enthalpy and Pressure of the Gas Mixture

Composition	
Propane	4.0%
Ethane	27.7%
Methane	39.5%
Nitrogen	28.8%

3.0 Gas Cleaning

Some progress has been made in the development of a suitable filter, capable of operating at room temperature, which could clean the hydrogen and helium gases to a level sufficient to prevent clogging of these stages during prolonged operation of the refrigerator. Previously it had been shown that purity levels in the parts per billion level were necessary for the case of water vapor in nitrogen. Similar purities can be obtained with the use of Zeolites when cooled to liquid nitrogen temperatures. However, for our purposes, where no liquid nitrogen would be used, the filter would have to be operated at ambient temperature.

Recently, a new organometallic resin has been announced which has been shown to be capable of removing most of the condensible impurities likely to be found in hydrogen and helium, to the parts per billion level at room temperature. This resin reacts instantly and irreversibly with the impurities to remove them from the gas stream. It is designed for low pressure operation and further work is needed before it can be used safely for cleaning gases in a J-T system. We are pursuing this and plan to test it in our high pressure filter package.

4.0.Refrigerator Redesign

4.1 Fabrication Difficulties

We have run into a serious problem in the fabrication of the hydrogen and helium stages of the three stage refrigerator. These stages differ from the first stage in that the size of the channels are much narrower than in the first stage. The lower molecular weight gases hydrogen and helium have very small viscosities and consequently, very narrow channels must be used in order to keep the mass flow to the design figure. Attempts to fabricate these fine channels have resulted in very poor yields. The problem is several fold. First, the etch rate at the bottom of a fine channel is much lower than that for a broad channel with the abrasive etching technique used in the fabrication of the refrigerators. As a result the resist can etch through before the channel is completely etched at the bottom, with the destruction of the bonding layer between the channels. Second, during the firing step the fine channels have collapsed before proper sealing can occur. This has been traced to variations in the thickness of the adhesive layer, which is screen printed on to the glass laminate. Better control is needed of the thickness of this layer. Thirdly, the space between the turns of the capillary in the hydrogen and helium stages had been kept to a few thousands of an inch to give a sufficiently long capillary. This is so narrow that it gives inadequate support for the resist between the channels under prolonged etching. A wider section is needed here.

We are addressing these problems in the following way:

We are working with a group at Stanford University to explore the possibility of sputtering the adhesive layer onto the glass. For layers of only a few microns thickness this should give much better control of the bonding layer thickness than can be obtained with screen printing. If this is successful we will acquire the necessary equipment to do the work in house at MMR.

We are redesigning the capillary sections to make them broader and shallower. With the thinner sputtered-on adhesive layer we should be able to avoid the problem of the adhesive flowing into the channels and blocking them. The broader channels will reduce the problems we have had with the etching, and with the shallower channels we can also use a shorter capillary with a greater width between the coils of the capillary.

At the same time we are making these modifications we will be incorporating changes in the design to utilise the added refrigeration capacity of the new gas mixture. This will allow the first stage to be shortened and a larger area devoted to the heat exchanger for the pre-cooling of the hydrogen and helium.

These changes to the capillary will first be made on the two stage prototype test refrigerator which we are using to check the heat exchanger design. This is much easier to fabricate and test than the full,circular refrigerator. Once this has been checked we will incorporate the changes in the final refrigerator.

5.0 Compressor Redesign

The experimental results obtained and the enthalpy figures calculated for the gas mixture

have shown that the first stage of he refrigerator can be designed for operation at 80 atm. rather than at 300 atm. as originally contemplated for with argon. This should have a dramatic effect on the life of the seals in this stage. The lower operating pressure also allows one to use a smaller hydraulic cylinder and a smaller hydraulic power source.

We have resized the drive cylinder. Using now a 1" diameter cylinder instead of 2". This entails some redesign of the mounting hardware and of the second stage cylinder mount. With the knowledge of the gas mixture performance now established, we are proceeding with the details of this design and fabrication of the three sub-systems of the compressor.

We have done some further testing of the prototype stage built earlier and have examined, in particular, the state of the valves. We had had some problem with the intake valve on the first stage when it was used at or below atmospheric pressure. However, this was due to some dirt on the seat and is not due to an intrinsic fault of the valve.

We have obtained literature on other available hydraulic power sources and lighter weight coolers and other hardware. While this is not of crucial importance yet, we want to determine what would be available and would will needto be developed specially for the system.

6.0 Personnel

The following persons have been involved in the program:

Gas Mixture Calculations

W. A. Little
A. E. Nash III
F. Kenter

Compressor Redesign

W. A. Little
H. Edman

Experimental Measurements

W. A. Little
M. Dubois

Refrigerator Fabrication

M. Stewart
F. Tochez
C. Fuentes

Respectfully submitted,

W. A. Little
President

END
11-87
DTIC